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PHOTOCURABLE COMPOSITIONS

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PHOTOCURABLE COMPOSITIONS

[Hikarikokasei soseibutsu]

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[Attached amendments have been incorporated in the translation.]

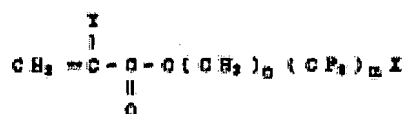
Specification

Claims

1. Photocurable compositions, characterized by comprising (a) monomers containing fluoroalkyl group and acrylic or methacrylic groups having at least one hydrogen atom per molecule, (b) fluorine-containing polymers, (c) crosslinkable monomers containing at least two polymerizable functional groups per molecule, and (d) photopolymerization initiators;

the photocurable compositions comprise 99-10 wt% component (a) plus component (c) compositions in which the weight ratio of component (a) to component (c) is from 99/1 to 1/1, 1-90 wt% component (b), and 0.1-10 weight parts component (d) based on 100 weight parts component (a) + component (b).

2. Photocurable compositions described in Claim 1, characterized in that compounds that can be represented by the following general formula



(where Y is H or CH<sub>3</sub>, n is an integer of 1 or greater, m is an integer of 1 or greater, and X is H, F or Cl) are used as the monomers of component (a).

### Detailed description of the invention

#### Industrial application field

The present invention relates to photocurable compositions with a controllable refractive index that can be used as adhesives, coating agents, sealing agents, etc. for optical communication, various optical instruments, etc.

#### Prior art and problems thereof

Generally speaking adhesives for optical instruments, for example, epoxy resins are known. The main components of such adhesives comprise epoxy resins and curing agents, and by changing the combination of these components, the refractive index, loss of optical transmittance, adhesive strength, flexibility, heat resistance, etc. have been adjusted to desired values. However, such adhesives that have been developed so far all have a high refractive index and when they are used for adhesion of, for example optical fibers, it is difficult to match their refractive index to that of optical fibers by changing the composition of the adhesives; therefore the reflection of optical signals at the joint ends of the optical fibers increases so that the signals are unstable and this is a problem. Generally the viscosity of epoxy resins prior to curing is high and once small air bubbles are present in epoxy resins, it is difficult to remove the air bubbles; such air bubbles change the optical properties of the adhesives very much and this is a problem.

#### Means to solve the problems

The present invention was devised to solve the above-mentioned problems and its essential point is in photopolymerizable compositions comprising (a) (meth)acrylate monomers containing fluoalkyl groups having at least one hydrogen atom per molecule,

(b) fluorine-containing polymers, (c) monomers having at least two polymerizable functional groups per molecule, and (d) photopolymerization initiators.

Examples of monomers constituting component (a) used at the time of carrying out the present invention include 1,1,2,2-tetrahydroperfluorododecyl (meth)acrylate, 1,1,2,2-tetrahydroperfluorodecyl (meth)acrylate, 1,1-dihydroperfluorobutyl (meth)acrylate, etc. and one or if necessary a mixture of at least two of these compounds may be used.

Examples of fluorine-containing polymers that constitute component (b) include homopolymers or copolymers of fluoroalkyl (meth)acrylate, homopolymers or copolymers of  $\alpha$ -fluoroacrylate, vinylidene fluoride polymers, vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene copolymers, etc. Among these polymers, from the viewpoint of transparency and refractive index, polymers or copolymers having fluoroalkyl (meth)acrylate as the main component are preferable. From the viewpoint of maintaining good photocuring properties and viscosity of the compositions and uniform and transparent compositions, the content of the fluorine-containing polymer in the compositions of the present invention is preferably 1-90 wt%.

Examples of multifunctional monomers of component (c) used in the present invention include 1,3-butanediol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, diethylene glycol diacrylate, neopentyl glycol diacrylate, polyethylene glycol diacrylate, tripropylene glycol diacrylate, hydroxypivalic acid ester neopentyl glycol diacrylate, neopentyl glycol-modified trimethylolpropane diacrylate; examples with three functional groups include trimethylolpropane triacrylate, pentaerythritol triacrylate, etc.; examples with five functional groups include dipentaerythritol monohydroxy pentaacrylate, etc.; and examples with six functional groups include dipentaerythritol hexaacrylate, etc. One or a mixture of at least two of the above-mentioned multifunctional crosslinking monomers may be used and the amount to be used is preferably 1-50 parts based on 100 parts monomer of component (a). If it is less than 1 part, it is difficult to obtain compositions having sufficient crosslinking density. Conversely if it is greater than 50 parts, the compatibility of the compositions drops and turbidity can be formed; thus it is not suitable.

For the photopolymerization initiators used in the present invention, generally the initiators and sensitizers for UV-curable coating materials can be used.

Examples include benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin butyl ether, 2-methylbenzoin, benzophenone, Michler's ketone, benzil, benzyl dimethyl ketal, benzyl diethyl ketal, anthraquinone, methylanthraquinone, diacetyl, acetophenone, diphenyl disulfide, anthracene, etc. and mixtures of these compounds and a small amount of sensitizer assistants such as amines. The amount of these photopolymerization initiators to be used is preferably 0.1-10 weight parts based on 100 weight parts monomer of

component (a). If it is less than 0.1 weight part, it is difficult to carry out sufficient initiation of polymerization, and on the other hand if it is greater than 10 weight parts the solubility in the compositions of the present invention is poor and no additional effect can be obtained from the increase in the amount used; thus it lacks practicality.

And other additives such as modifiers for improving adhesion may be added within the scope wherein curing conditions and compatibility are allowable.

#### Effect of the invention

The refractive index of the cured products of the present invention can be controlled and the refractive index of the cured products closely matches the refractive index of optical fibers, ~~optical lens~~, etc. and the cured products have good heat resistance, flexibility, and adhesive properties.

And the photocurable compositions of the present invention are excellent in curing rate and controllability of the viscosity of uncured compositions; thus they can be modified freely depending on the use.

In the following, the present invention will be explained in more detail using application examples.

#### Application Example 1

A photocurable composition was obtained by mixing 20 weight parts 1,1,2,2-tetrahydroperfluorodecyl acrylate as monomer (a), 80 weight parts trifluoroethyl acrylate, 7 weight parts 1,6-hexanediol diacrylate as a multifunctional monomer, 15 weight parts copolymer comprising 38 wt% trifluoroethyl methacrylate and 62 wt% 1,1,2,2-tetrahydroperfluorodecyl methacrylate, and 3 weight parts benzil methyl ketal (trade name; Irgacure 651, Ciba-Geigy Corp.) as a photopolymerization initiator. The composition was cast at a thickness of 100  $\mu\text{m}$  on a glass plate and covered tightly with a polyester film to give a sample. The sample was irradiated for about 1 second with 80 W/cm energy using a UV ray exposing apparatus having a built-in high-pressure mercury lamp to obtain a cured product.

The cured product was a flexible and transparent film having a refractive index of 1.389. The transparency of the film did not change even after the film was heated at 150°C for 20 h.

#### Application Examples 2-5

Cured products were obtained by carrying out the procedure of Application Example 1 except that the photocurable compositions were changed as shown in Table 1. The refractive index and Shore hardness of the cured products are shown in Table 1. All of the photocurable

composition films were transparent and flexible. There was no change in the transparency of films after the films were heated at 150°C for 20 h.

Table 1

①	② 硬化性組成物	⑤	⑥	⑦
①	実施例 2 $\text{CH}_2 = \text{CHCOOCH}_2$ ②, $\text{C}_6\text{F}_5$ , $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOCH}_2(\text{CF}_3)$ , $\text{H}$ の重合体 ③ $(\text{CH}_2 = \text{CHCOOCH}_2)$ , $\text{C}_6\text{F}_5$ , $\text{CH}_2 = \text{CHCOOCH}_2, \text{C}_6\text{F}_5$	00 60 5 30	1.395	93
①	実施例 3 $\text{CH}_2 = \text{CHCOOCH}_2, \text{CF}_3$ の重合体 ③ $\text{CH}_2 = \text{CHCOO}(\text{CH}_2)_2, \text{OCOCH} = \text{CH}_2$ $\text{CH}_2 = \text{CHCOOCH}_2, \text{CH}_2, \text{C}_6\text{F}_5$ ④	60 10 80	1.415	98
①	実施例 4 $\text{CH}_2 = \text{CHCOOCH}_2, (\text{CF}_3)_2\text{CH}$ (93重量%) $\text{CH}_2 = \text{CHCOOCH}_2, (\text{CF}_3)_2\text{CH}$ (3重量%) $\text{CH}_2 = \text{CHCOOCH}_2, \text{CF}_3$ ④ $\text{CH}_2 = \text{CHCOO}(\text{CH}_2)_2, \text{OCOCH} = \text{CH}_2$ $\text{CH}_2 = \text{CHCOOCH}_2, \text{CH}_2, \text{C}_6\text{F}_5$ $\text{CH}_2 = \text{CHCOOCH}_2, (\text{CF}_3)_2\text{CH}$ ④	10 7 20 10 40	1.390	80
①	実施例 5 $\text{CH}_2 = \text{CHCOOCH}_2$ ④ $\text{CH}_2 = \text{CF}_2$ (68重量%) $\text{CF}_2 = \text{CF}_2$ (32重量%) の共重合体 ③ $\text{CH}_2 = \text{CHCOO}(\text{CH}_2)_2, \text{OCOCH} = \text{CH}_2$	15 15	1.447	75

Key: 1 Application Example  
 2 Photocurable composition  
 3 Polymer of  
 4 Wt%  
 5 Weight parts  
 6 Refractive index  
 7 Shore hardness

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